UNITED STATES PATENT APPLICATION FOR:

STABILIZATION OF ADDITIVES CONCENTRATION IN ELECTROPLATING BATHS FOR INTERCONECT FORMATION

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STABILIZATION OF ADDITIVES CONCENTRATION IN ELECTROPLATING BATHS FOR INTERCONECT FORMATION

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] Embodiments of the invention generally relate to an apparatus and method for dosing additives into an electrochemical plating cell to maintain a desired additive concentration.

Description of the Related Art

[0002] Metallization of sub-quarter micron sized features is a foundational technology for present and future generations of integrated circuit manufacturing processes. More particularly, in devices such as ultra large scale integration-type devices, *i.e.*, devices having integrated circuits with more than a million logic gates, the multilevel interconnects that lie at the heart of these devices are generally formed by filling high aspect ratio, *i.e.*, greater than about 4:1, interconnect features with a conductive material, such as copper or aluminum. Conventionally, deposition techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) have been used to fill these interconnect features. However, as the interconnect sizes decrease and aspect ratios increase, void-free interconnect feature fill via conventional metallization techniques becomes increasingly difficult. Therefore, plating techniques, *i.e.*, electrochemical plating (ECP) and electroless plating, have emerged as promising processes for void free filling of sub-quarter micron sized high aspect ratio interconnect features in integrated circuit manufacturing processes.

[0003] In an ECP process, for example, sub-quarter micron sized high aspect ratio features formed into the surface of a substrate (or a layer deposited thereon) may be efficiently filled with a conductive material, such as copper. ECP plating processes are generally two stage processes, wherein a seed layer is first formed over the surface features of the substrate, and then the surface features of the

substrate are exposed to an electrolyte solution, while an electrical bias is applied between the seed layer and a copper anode positioned within the electrolyte solution. The electrolyte solution generally contains ions to be plated onto the surface of the substrate, and therefore, the application of the electrical bias causes these ions to be urged out of the electrolyte solution and to be plated onto the biased seed layer.

[0004] Conventional chemical plating cells generally utilize an overflow weir-type plater containing a plating solution, which is also generally termed a catholyte herein. The substrate is positioned at the top of the weir during plating and an electrical plating bias is applied between the substrate and an anode positioned on a lower portion of the plating solution. This bias causes metal ions in the plating solution to go through a reduction that causes the ions to be plated on the substrate. However, one challenge associated with conventional plating cells is that the plating solution contains additives that are configured to control the plating process, and these additives are known to react with the anode during plating processes. This reaction with the anode causes the additives to breakdown, which generally renders the additives ineffective. Further, when the additives breakdown and are no longer able to facilitate process control, then the additives essentially become contaminants in the plating solution. As such, the concentration of the additives in the plating is constantly varying as a result of consumption in the plating process. This consumption of additives is generally addressed via a dosing mechanism configured to dose additives into the plating solution in response to consumption. However, one challenge associated with the dosing methodology is that it is difficult to maintain a constant concentration of additives, as the measurement and dosing processes take a substantial amount of time. Therefore, by the time the measurement is taken and the bath is dosed, the concentration has already changed. As such, the dosing system tends to chase the desired concentrations and is subject to substantial fluctuation.

[0005] Another challenge associated with conventional plating cells is that the consumption of additives by the plating process also generates breakdown products.

These breakdown products are a result of the additives being used or depleted, and generally these breakdown products increase in concentration in the plating solution with time. Further, the breakdown products have been shown to increase plating defects.

[0006] Therefore, there is a need for a method and apparatus for controlling additive concentrations and breakdown concentrations in electrochemical plating cells.

SUMMARY OF THE INVENTION

[0007] Embodiments of the invention provide an electrochemical plating cell. The plating cell includes a fluid basin having an anolyte solution compartment and a catholyte solution compartment, an ionic membrane positioned between the anolyte solution compartment and the catholyte solution compartment, and an anode positioned in the anolyte solution compartment, wherein the ionic membrane comprises a poly tetrafluoroethylene based ionomer.

[0008] Embodiments of the invention may further provide a method for maintaining an additive concentration in an electrochemical plating solution within a processing window. The method includes positioning a container having a fluid inlet and a fluid outlet in fluid communication with a fluid conduit connecting a plating cell and a fluid supply tank, saturating an absorbent material positioned in an interior of the container with the additive, dispensing the additive from the absorbent material when a concentration of the additive in the plating solution is below a desired concentration, and absorbing the additive from the plating solution into the absorbent material when the concentration of the additive in the plating solution is above the desired concentration.

[0009] Embodiments of the invention may further provide an electrochemical plating cell. The cell includes a fluid basin configured to contain an electrolyte plating solution, a fluid tank in fluid communication with the fluid basin and being configured to supply the electrolyte plating solution thereto, and an electrolyte solution stabilization device in fluid communication with the fluid tank. The

stabilization device includes a fluid container having a fluid inlet and a fluid outlet, and an absorbent material positioned in the fluid container in a fluid path between the fluid inlet and the fluid outlet, wherein the absorbent material is configured to leach a solution additive into the electrolyte plating solution to maintain the solution additive within a processing window during an electrochemical plating process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0011] Figure 1 is a top plan view of an exemplary electrochemical plating system of the invention.

[0012] Figure 2 illustrates a sectional view of an exemplary plating cell of the invention.

[0013] Figure 3 illustrates a sectional view of another exemplary electrochemical plating cell of the invention.

[0014] Figure 4 illustrates an exemplary plumbing configuration for an electrochemical plating cell of the invention.

[0015] Figure 5 illustrates another exemplary plumbing configuration for an electrochemical plating cell of the invention.

[0016] Figure 6 illustrates a graph of the relationship between additive concentration changes in a plating cell during plating operations.

[0017] Figure 7 illustrates a graph of additive and breakdown concentration changes in the electrolyte tank under cell operation with a dosing process active.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0018] Embodiments of the invention generally provide and electrochemical plating system, wherein the electrochemical plating cells of the system includes an apparatus and/or method for dosing additives into the electrochemical plating solution with minimal concentration variation. Embodiments of the invention also provide an apparatus and method for preventing the additive breakdown concentration from increasing over time. The combination of maintaining a relatively constant additive concentration in conjunction with minimizing the breakdown concentration increase provides a plating cell that is capable of substantially eliminating plating defects resulting from additive dosing and breakdown.

[0019] Figure 1 illustrates a top plan view of an ECP system 100 of the invention. ECP system 100 includes a factory interface (FI) 130, which is also generally termed a substrate loading station. Factory interface 130 includes a plurality of substrate loading stations configured to interface with substrate containing cassettes 134. A robot 132 is positioned in factory interface 130 and is configured to access substrates contained in the cassettes 134. Further, robot 132 also extends into a link tunnel 115 that connects factory interface 130 to processing mainframe or platform 113. The position of robot 132 allows the robot to access substrate cassettes 134 to retrieve substrates therefrom and then deliver the substrates to one of the processing cells 114, 116 positioned on the mainframe 113, or alternatively, to the annealing station 135. Similarly, robot 132 may be used to retrieve substrates from the processing cells 114, 116 or the annealing chamber 135 after a substrate processing sequence is complete. In this situation robot 132 may deliver the substrate back to one of the cassettes 134 for removal from system 100. Additional configurations and implementations of an electrochemical processing system are illustrated in commonly assigned United States Patent Application Serial No. 10/435,121 filed on December 19, 2002 entitled "Multi-Chemistry Electrochemical Processing System", which is incorporated herein by reference in its entirety.

[0020] The anneal chamber 135 generally includes a two position annealing chamber, wherein a cooling plate/position 136 and a heating plate/position 137 are positioned adjacently with a substrate transfer robot 140 positioned proximate thereto, *e.g.*, between the two stations. The robot 140 is generally configured to move substrates between the respective heating 137 and cooling plates 136. Further, although the anneal chamber 135 is illustrated as being positioned such that it is accessed from the link tunnel 115, embodiments of the invention are not limited to any particular configuration or placement. As such, the anneal chamber may be positioned in communication with the mainframe 113. Additional information relative to the anneal chamber of the invention may be found in a commonly assigned U.S. Patent Application entitled "Two Position Anneal Chamber" naming Edwin Mok and Son Nguyen as inventors (serial number unavailable at the time of filing), which is hereby incorporated by reference in its entirety.

[0021] As mentioned above, ECP system 100 also includes a processing mainframe 113 having a substrate transfer robot 120 centrally positioned thereon. Robot 120 generally includes one or more arms/blades 122, 124 configured to support and transfer substrates thereon. Additionally, the robot 120 and the accompanying blades 122, 124 are generally configured to extend, rotate, and vertically move so that the robot 120 may insert and remove substrates to and from a plurality of processing locations 102, 104, 106, 108, 110, 112, 114, 116 positioned on the mainframe 113. Similarly, factory interface robot 132 also includes the ability to rotate, extend, and vertically move its substrate support blade, while also allowing for linear travel along the robot track that extends from the factory interface 130 to the mainframe 113. Generally, process locations 102, 104, 106, 108, 110, 112, 114, 116 may be any number of processing cells utilized in an electrochemical plating platform. More particularly, the process locations may be configured as electrochemical plating cells, rinsing cells, bevel clean cells, spin rinse dry cells, substrate surface cleaning cells, electroless plating cells, metrology inspection stations, and/or other processing cells that may be beneficially used in conjunction with a plating platform. Each of the respective processing cells and robots are generally in communication with a process controller 111, which may be a

microprocessor-based control system configured to receive inputs from both a user and/or various sensors positioned on the system 100 and appropriately control the operation of system 100 in accordance with the inputs.

[0022] In the exemplary plating system illustrated in Figure 1, the processing locations may be configured as follows. Processing locations 114 and 116 may be configured as an interface between the wet processing stations on the mainframe 113 and the dry processing regions in the link tunnel 115, annealing chamber 135, and the factory interface 130. The processing cells located at the interface locations may be spin rinse dry cells and/or substrate cleaning cells. More particularly, each of locations 114 and 116 may include both a spin rinse dry cell and a substrate cleaning cell in a stacked configuration. Locations 102, 104, 110, and 112 may be configured as plating cells, either electrochemical plating cells or electroless plating cells, for example. Locations 106, 108 may be configured as substrate bevel cleaning cells. Additional configurations and implementations of an electrochemical processing system are illustrated in commonly assigned United States Patent Application Serial No. 10/435,121 filed on December 19, 2002 entitled "Multi-Chemistry Electrochemical Processing System", which is incorporated herein by reference in its entirety.

[0023] Figure 2 illustrates a partial perspective and sectional view of an exemplary plating cell 200 that may be implemented in processing locations 102, 104, 110, and 112. The electrochemical plating cell 200 generally includes an outer basin 201 and an inner basin 202 positioned within outer basin 201. Inner basin 202 (also referred to as a weir) is generally configured to contain a plating solution that is used to plate a metal, *e.g.*, copper, onto a substrate during an electrochemical plating process. During the plating process, the plating solution is generally continuously supplied to inner basin 202 (at about 1 gallon per minute for a 10 liter plating cell, for example), and therefore, the plating solution continually overflows the uppermost point or weir of inner basin 202 and is collected by outer basin 201 and drained therefrom for chemical management and recirculation. Plating cell 200 is generally positioned at a tilt angle, *i.e.*, the frame portion 203 of plating cell 200 is

generally elevated on one side such that the components of plating cell 200 are tilted between about 3° and about 30°, or generally between about 4° and about 10° for optimal results. The frame member 203 of plating cell 200 supports an annular base member on an upper portion thereof. Since frame member 203 is elevated on one side, the upper surface of base member 204 is generally tilted from the horizontal at an angle that corresponds to the angle of frame member 203 relative to a horizontal position. Base member 204 includes an annular or disk shaped recess formed into a central portion thereof, the annular recess being configured to receive a disk shaped anode member 205. Base member 204 further includes a plurality of fluid inlets/drains 209 extending from a lower surface thereof. Each of the fluid inlets/drains 209 are generally configured to individually supply or drain a fluid to or from either the anode compartment or the cathode compartment of plating cell 200. Anode member 205 generally includes a plurality of slots 207 formed therethrough, wherein the slots 207 are generally positioned in parallel orientation with each other across the surface of the anode 205. The parallel orientation allows for dense fluids generated at the anode surface to flow downwardly across the anode surface and into one of the slots 207.

[0024] Plating cell 200 further includes a membrane support assembly 206. Membrane support assembly 206 is generally secured at an outer periphery thereof to base member 204, and includes an interior region configured to allow fluids to pass therethrough. A membrane 208 is stretched across the support 206 and operates to fluidly separate a catholyte chamber and anolyte chamber portions of the plating cell. The membrane support assembly may include an o-ring type seal positioned near a perimeter of the membrane, wherein the seal is configured to prevent fluids from traveling from one side of the membrane secured on the membrane support 206 to the other side of the membrane. A diffusion plate 210, which is generally a porous ceramic disk member is configured to generate a substantially laminar flow or even flow of fluid in the direction of the substrate being plated, is positioned in the cell between membrane 208 and the substrate being plated. The exemplary plating cell is further illustrated in commonly assigned United States Patent Application Serial No. 10/268,284, which was filed on October 9, 2002

under the title "Electrochemical Processing Cell", claiming priority to United States Provisional Application Serial No. 60/398,345, which was filed on July 24, 2002, both of which are incorporated herein by reference in their entireties.

[0025] Membrane 208 generally operates to fluidly isolate the anode chamber from the cathode chamber of the plating cell. Membrane 208 is generally an ionic or ion exchange membrane. The ion exchange membrane generally includes fixed negatively charged groups, such as $-SO_3$, -COO, HPO_{2-}, SeO_{3-}, PO_{32-}, or other negatively charged groups amenable to plating processes. Membrane 208 allows a particular type of ions to travel through the membrane, while preventing another type of ion from traveling or passing through the membrane. More particularly, membrane 208 may be a cationic membrane that is configured to allow positively charged copper ions (Cu^{2+}) to pass therethrough, *i.e.*, to allow copper ions to travel from the anode in the anolyte solution through the membrane 208 into the catholyte solution, where the copper ions may then be plated onto the substrate. Further, the cationic membrane may be configured to prevent passage of negatively charged ions and electrically neutral species in the solution, such as the ions that make up the plating solution and catholyte additives. It is desirable to prevent these catholyte additives from traveling through the membrane 208 and contacting the anode, as the additives are known to break down upon contacting the anode. More particularly, membranes with negatively charged ion groups like SO3- etc. not only to facilitate Cu ions transport from the anolyte to the catolyte, but also to prevent penetration of accelerators to anode. The accelerator is generally negatively charged organic ion: $^-$SO3- C3H6-S-S-C3H6-SO3$^-$, so it can't penetrate into or through the cation membrane. Further details of the membrane configuration of the plating cell may be found in commonly assigned United States Patent Application entitled "ELECTROCHEMICAL PROCESSING CELL", under attorney docket number APPM/7669.P3, naming Michael X. Yang, Dmitry Lubomirsky, Yesdi N. Dordi, Saravjeet Singh, Sheshraj L. Tulshibagwale, and Nicolay Kovarsky as inventors, which is hereby incorporated by reference in its entirety.

[0026] Figure 3 illustrates a sectional view of another electrochemical plating cell 300 of the invention. The electrochemical plating cell illustrated in Figure 3 is similar to the plating cell illustrated in Figure 2, however, the plating cell in Figure 3 does not include a separate anolyte and catholyte compartments. More particularly, the plating cell illustrated in Figure 3 utilizes a single plating solution, *i.e.*, a catholyte plating solution, while the plating cell of Figure 2 uses both a catholyte and an anolyte solution, which are separated by the membrane 208. ECP system 300 generally includes a head assembly actuator 302, a substrate holder assembly 310, and a plating basin assembly 360. The head actuator assembly 302 is generally attached to a supporting base 304 by a pivotally mounted support arm 306. The head actuator assembly 302 is adapted to support the substrate holder assembly 310 (also generally referred to as an ECP contact ring) at various positions above the plating basin 360, and more particularly, the actuator assembly 302 is configured to position the substrate holder assembly 310 into a plating solution contained within basin 360 for plating operations. Head actuator 302 may generally be configured to rotate, vertically actuate, and tilt the substrate holder assembly 310 attached thereto before, during, and after the substrate 120 is placed in the plating solution.

[0027] The plating basin 360 generally includes an inner basin 362, contained within a larger diameter outer basin 364. Any suitable technique may be used to supply a plating solution to the plating assembly 360. For example, a plating solution may be supplied to the inner basin 362 through an inlet 366 at a bottom surface of the inner basin 362. The inlet 366 may be connected to a supply line, for example, from an electrolyte reservoir system (not shown). The outer basin 364 may operate to collect fluids from the inner basin 362 and drain the collected fluids via a fluid drain 368, which may also be connected to the electrolyte reservoir system and configured to return collected fluids thereto.

[0028] An anode assembly 370 is generally positioned in a lower region of inner basin 362. A diffusion member 372 may be generally positioned across the diameter of inner basin at a position above the anode assembly 370. The anode assembly 370 may be any suitable consumable or non-consumable-type anode,

e.g., copper, platinum, etc. The diffusion member 372 may be any suitable type of permeable material, such as a porous ceramic disk member, for example. The diffusion member 372 is generally configured to generate an even flow of electrolyte solution therethrough in the direction of the substrate being plated, and further, to provide a degree of control over the electrical flux traveling between the anode and the substrate being plated. Any suitable method may be used to provide an electrical connection to the anode assembly 370. For example, an electrical connection to the anode assembly 370 may be provided through an anode electrode contact 374. The anode electrode contact 374 may be made from any suitable conductive material that is insoluble in the plating solution, such as titanium, platinum and platinum-coated stainless steel. As illustrated, the anode electrode contact 374 may extend through a bottom surface of the plating bath assembly 360 and may be connected to an electrical power supply (not shown), for example, through any suitable wiring conduit.

[0029] As noted above, stabilization of additive concentrations in the electrochemical plating bath is a key component to maintaining acceptable plating defect ratios. As such, embodiments of the invention utilize a novel plumbing and additive adsorption and desorption process to maintain the additive concentrations at their desired levels. More particularly, Figure 4 illustrates an exemplary plumbing configuration for an electrochemical plating cell of the invention. The plumbing configuration illustrates a plating cell 400 in the fluid communication with an electrolyte supply tank 404. The plating sell 400 includes a substrate support member configured to support a substrate 401 for processing, a porous diffusion member 403 positioned across the plating cell 400, and an anode 402 positioned in a lower portion of the plating cell 400. A plating solution or a catholyte solution is supplied to the plating cell by a fluid supply conduit 411 and returned to the electrolyte supply tank 404 via a return conduit 412. The return conduit 412 includes an absorbent container 403 and a filter 406. Filter 406, which may generally be a fluid permeable filter configured to trap particulates, operates to prevent the electrolyte entering the electrochemical cell from containing small absorbent

particles that can penetrate into the electrolyte stream. Fluid pressure may be provided to both the supply and return conduits via a pump 407.

[0030] Figure 5 illustrates another exemplary plumbing configuration for electrochemical plating cell of the invention. Plating cell 500 again includes the ability to support a substrate 501, a diffusion member 503, and an anode 502. However, in this configuration the filter 506 and pump 507 are positioned between the electrolyte supply tank 504 and the plating cell 500. Additionally, the absorbent container 505 is positioned in a lower portion of the electrolyte supply tank 504. Additionally, figure 5 illustrates the positioning of a membrane 510 within the plating cell 500, along with an anolyte solution circulation loop 515. Although Figures 4 and 5 illustrate exemplary plumbing configurations in communication with various plating cells, *i.e.*, plating cells with and without membranes and with and without catholyte loops, embodiments of the invention are not intended to be limited to any particular plumbing configuration or plating cell configuration.

[0031] The catholyte or plating solution contained in tanks 404,504 (the solution used to contact and plate metal/copper onto the substrate) generally includes several constituents. The constituents generally include a virgin makeup plating solution (a plating solution that does not contain and plating additives, such as levelers, suppressors, or accelerators, such as that provided by Shipley Ronal of Marlborough, MA or Enthone, a division of Cookson Electronics PWB Materials & Chemistry of London), water (generally included as part of the VMS, but is may also be added), and a plurality of plating solution additives configured to provide control over various parameters of the plating process. The catholyte is generally a low acid-type of plating solution, *i.e.*, the catholyte generally has between about 5g/L of acid and about 150 g/L of acid, or more particularly, between about 5 g/L and about 30 g/L. The acid may be sulfuric acid, sulfonic acid (including alkane sulfonic acids), pyrophosphoric acid, citric acid, and other acids known to support electrochemical plating processes. The desired copper concentration in the catholyte is generally between about 25 g/L and about 70 g/L, preferably between about 30 g/L and about 50 g/L of copper. The copper is generally provided to the solution via copper

sulfate, and/or through the electrolytic reaction of the plating process wherein copper ions are provided to the solution via the anolyte from a soluble copper anode positioned in the catholyte solution. More particularly, copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) may be diluted to obtain a copper concentration of about 40 g/L, for example. A common acid and copper source combination is sulfuric acid and copper sulfate, for example. The catholyte also has chloride ions, which may be supplied by hydrochloric acid or copper chloride, for example, and the concentration of the chlorine may be between about 30 ppm and about 60 ppm.

[0032] As noted above, the plating solution (catholyte) generally contains one or more plating additives configured to provide a level of control over the plating process. The additives may include suppressors at a concentration of between about 1.5 mL/L and about 6 mL/L, preferably between about 2 mL/L and 4.0 mL/L. Exemplary suppressors include ethylene oxide and propylene oxide copolymers. Additives may also include accelerators at a concentration of between about 3 mL/L and about 10 mL/L, preferably within the range of between about 4.5 mL/L and 8.5 mL/L. Exemplary accelerators are based on sulfopropyl-disulfide or mercapto-propane-sulphonate and their derivatives.

[0033] Additionally, another additive that may optionally be added to the catholyte solution is a leveler at a concentration of between about 1 mL/L and about 12 mL/L, or more particularly, in the range of between about 1.5 mL/L and 4 mL/L

[0034] The anolyte solution (the solution supplied to the anolyte loop illustrated in Figure 5 and Figure 2) is generally contained in the volume below the membrane 208 and above the anode. The anolyte solution may be simply the catholyte solution without the plating additives, *i.e.*, levelers, suppressors, and/or accelerators. However, the inventors have found that specific anolyte solutions, other than just stripped catholyte solutions, provide a substantial improvement in plating parameters. Specifically, copper transfer through the membrane and prevention of copper sulfate and hydroxide precipitation, *i.e.*, when the Cu ions transport through membrane, copper sulfate accumulates in the anolyte and starts to precipitate on

the anode provoking its passiviation are improved. When pH of the anolyte is maintained above about 4.5 to about 4.8, copper hydroxide starts to deposit from Cu salt solutions, *i.e.*, $Cu^{2+} + 2H_2O = Cu(OH)_2$ (deposit) + $2H^+$. More particularly, the inventors have found that if the anolyte can be configured to supply between about 90% and about 100% of the copper to the catholyte, then the membrane essentially operates as a clean copper anode, *i.e.*, the membrane provides copper to the catholyte without the disadvantages associated with the electrochemical reaction that takes place at the surface of the anode (sludge formation, additive consumption, planarity variations due to erosion, etc.). The anolyte of the invention generally includes a soluble copper II salt (copper ions are not complexed with ligands like NH_3, or EDTA or phyrophoshoric acid anions, as Cu transports through the membrane together with this ligand, like $Cu(NH_3)_4^{2+}$ will transport together with NH_3, such as copper sulfate, copper sulfonate, copper chloride, copper bromide, copper nitrate, or a blend of any combination of these salts in an amount sufficient to provide a concentration of copper ions in the catholyte of between about 0.1M and about 2.5M, or more particularly, between about 0.25 M and about 2M.

[0035] Additionally, the pH of the anolyte solution will generally be between about 1.5 and about 6, or more particularly, between about 2 and 4.8, for example. The pH is maintained in this range, as increasing the pH above this range in conventional plating configurations has been shown cause copper hydroxide precipitation. Additionally, when the pH is below 2, and particularly if the pH is below 1.5, then the solution supports a substantial increase in the hydrogen ion (H^+) transport through the membrane from the anolyte to the catholyte. In this situation, the bulk of the plating current is carried by the H^+ ions and the copper ion transport is reduced. As such, the copper ion concentration in the catholyte decreases, potentially to a critical level that will not support plating, while simultaneously the sulfuric acid concentration in the catholyte increases. The anolyte can generally use any soluble Cu^{2+} salt, such as $CuSO_4$ (solubility 300 g/L), $CuBr_2$ (solubility more that 2 kg/L), $CuCl_2$ (solubility 700 g/L), CuF_2(47 g/L), $Cu(NO_3)_2$ (1300 g/L) etc. The selection of anions depends on their impact to prevent or minimize Cu(I) formation and anode passiviation, on penetration through the membrane etc. For instance,

the anolyte can be $CuSO_4$ (0.5M) with small additions of $Cu(NO_3)$ to activate anode surface and minimize Cu(I) formation). To minimize Cu(I) formation, small additions of $Cu(ClO_3)_2$ (solubility 2 kg/L) or $Cu(IO_3)_2$ – solubility 1 g/L may be used. In similar fashion to the catholyte, the source of copper in the anolyte (aside from the anode) may be cupper sulfate pentahydrate ($CuSO_4{\bullet}5H_2O$) at between about 32 g/L and 70 g/L, or at between about 0.5M and about 0.95M. Alternatively, in a preferred embodiment, the copper source may be between about 51 g/L and about 60 g/L, preferably about 54 g/L, and at a molarity of between about 0.8M and about 0.9M, preferably about 0.85M.

[0036] The absorbent containers 404, 504 (illustrated in Figures 4 and 5) generally include an enclosed container column with at least one fluid inlet and at least one fluid outlet. The fluid path between the fluid inlet and the fluid outlet traverses an absorbent material positioned in the container or column, wherein the absorbent material is configured to contain one or more of the plating solution additives (catholyte additives, *i.e.*, levelers, suppressors, accelerators, etc.). The absorbent material is generally absorbent to the additives, and as such, the absorbent material may be saturated with the one or more additives prior to initiating the plating process. Once saturated or otherwise provided with one or more additives, the absorbent material is generally configured to desorb the additives contained therein at a known rate. More particularly, the absorbent material may be configured to desorb additives contained therein at a rate that is proportional to the fluid flow through the container or column. Alternatively, the absorbent material may leach additives in proportion to the fluid pressure applied to the container or column. Regardless of the control method for the additive desorption, when the additive concentration in the absorbent material and the additive concentration in the plating solution are equilibrated with one another, the following equation can be used:

$$CX + CY + CZ \leftrightarrow CaX + CaY + CaZ,$$

wherein CX , CY, and CZ represent the concentrations of additives X, Y, and Z in the electrolyte, CaX, CaY, and CaZ represent concentrations of additives in the

absorbent material under equilibrium, and wherein ↔ represents absorption and desorption of the additives (adsorption is the rightward facing arrow and desorption is the leftward facing arrow). For example, at a given temperature and given concentrations of primary chemicals into electrolyte (e.g. 50 g/L $CuSO_4$, 30 g/L H_2SO_4), there is only one combination of CaX1, CaY1, and CaZ1 for each combination of CX1, CY1, and CZ1. The rate of adsorption (Ka) and the rate of desorption (Kd) under equilibrium are equal to one another. When one will add additional amount of absorbent (saturated with these additives at CX1, CY1, and CZ1) or additional volume of the same electrolyte into this system, all concentrations remain the same. However, when the concentration of any additive (e.g. X) in the electrolyte decreases (because of consumption, decomposition etc.), it immediately rises the desorption of X from absorbent so that the concentration of Cx in the electrolyte increases to the same value as it was before. Similarly, when the concentration of the additive increases (e.g. because of incorrect dosing, *i.e.*, from overdosing), the absorbent starts to adsorb the excess and the Cx value returns to the initial value. Thus, not only does the absorbent material operate to dispense additives into the solution, it also operates like a buffer, as it operates to compensate for changes of Cx (or other additives) into the electrolyte, thus keeping the Cx value near a desired concentration. However, in similar fashion to most buffers, the adsorbent is only capable of buffering within a proper limit. One parameter that may influence this characteristic is the ratio of the volume of the adsorbent material to the volume of the solution, *i.e.*, the higher is the adsorption capacity of absorbent regarding to X, the higher is the absorbent-to-electrolyte volume ratio and the lower is the Cx that must be maintained, the better and longer the absorbent can keep the required concentration of additive into the electrolyte bulk.

[0037] For example, during the initial plating process, both the electrolyte and absorbent material contains only additives X, Y, and Z, but during electrolysis these additives decompose on the electrodes and the concentration of breakdown products of X, Y, and Z (CBX, CBY, CBZ) into electrolyte increases. At the same time, the absorbent starts to absorb these breakdown products, decreasing their concentration into the electrolyte, which leads to substantial increase in electrolyte

life-time, because the capacity of adsorbent relative to breakdown products will generally be approximately the same as X, Y, and Z.

[0038] Figure 5 illustrates concentration changes of an exemplary additive X in the electrolyte or plating solution under electrolysis both when it is in contact with an absorbent saturated with additives and when there is no absorbent into the system. As illustrated in Figure 5, the presence of the absorbent material saturated with additives (generally the absorbent-electrolyte volume ratio will be between about 1:1 and about 1:10) maintains the concentration of the additives relatively constant for several days without any correction of the electrolyte, whereas without the absorbent material the concentration varies out of the processing range after several hours of electrolysis. At the same time, the accumulation of breakdown products into electrolyte becomes much slower with the absorbent material. This system (high absorbent-electrolyte volume ratio) is especially helpful when the electrolyte volume used is relatively low and there is no chemical control system that can correct additive concentration. This system provides a substantial increase in the lifetime of the electrolyte without any concentration control and correction and without any care about accumulation of breakdown into the electrolyte. After several days when the capacity of absorbent becomes exhausted, the electrolyte and adsorbent may be replaced by fresh materials.

[0039] Figure 7 illustrates a graph of additive and breakdown concentration changes in the electrolyte tank under cell operation with a dosing process active. More particularly, Figure 7 illustrates a graph of the situation when the absorbent electrolyte volume ratio is relatively low, less than about 1:10. In this case the capacity of absorbent material is not enough to keep the initial concentration of X (CX0) for long periods of time under electrolysis, so the chemical cabinet that controls and feeds the electrolyte by additives is required. However, the presence of the additive saturated absorbent in the system assists in maintaining a constant additive concentration. This configuration also provides several advantages, *i.e.*, the capacity of the absorbent remains sufficient to keep the CXO within the desired window for several hours even when the system is not fed by fresh X, as the

buffering (additive leaching) properties of the absorbent material operates to minimize the concentration fluctuations (which generally arise in response to dosing). Therefore, for example, when the chemical cabinet is inoperable for whatever reason or when there is another kind of operational fault in the chemical dosing hardware, the absorbent material provides an alternative dosing source for a period of time. This allows the user to continue processing substrates (plating) without having shut down the electrodeposition tool as a result of a chemical cabinet failure, as the absorbent material is sufficient to maintain acceptable additive concentrations for a substantial period of time. Additionally, the adsorbent also operates to extract breakdown products and at the same time desorbs fresh additives into electrolyte, thus greatly increasing the usable lifetime of electrolyte.

[0040] The canister, container, column, etc. containing the absorbent material, i.e., container 405 or 505 in Figures 4 and 5, as noted above, generally includes a housing having a fluid inlet and a fluid outlet with the absorbent material positioned in the fluid path between the inlet and the outlet. The electrolyte supply may then be fed into the fluid inlet and passed through the absorbent material before exiting the container at the fluid outlet. The supply of electrolyte to the container may be through a slipstream-type configuration, for example. During the process of the fluid flowing from the inlet to the outlet, the absorbent material leaches a portion of the additives contained therein into the fluid solution flowing therethrough. Exemplary absorbent materials include activated carbon and charcoal, various polymers (e.g. polypropylene), glass, minerals, ion-exchange resins, resins for chromatography, and combinations thereof. These materials may be used in various forms within the canister, column, container, etc., *i.e.*, they may be in the form of beads, granules, pellets, powder, fabric pads, rolls, fibers, etc). Generally, the only limitations imposed upon the absorbent material is that the material should be chemically stable in the electrolyte plating solutions, and the material should have the ability ot be cleaned from any kind of particles or chemical components (ions, salts or organic molecules) that can contaminate the electrolyte and are detrimental to plating processes.

[0041] In operation, the implementation of the canisters of the invention containing the absorbent material may be positioned either in a fluid supply line (as illustrated in Figure 4, in an electrolyte tank (as illustrated in Figure 5), or alternatively, in the electroplating cell itself (not shown). The absorbent material is used to supply plating solution additives to the plating solution when the concentration of the additives in the solution is lower than a desired concentration. Similarly, when the concentration of the additives in the solution is higher than a desired level, then the absorbent material is configured to absorb additives from the electrolyte solution, this lowering the concentration of the additives in the solution to within the desired range. As such, the absorbent material operates to maintain the plating solution additive concentration within the desired processing range, even in the presence of concentration fluctuations that are often present in plating systems as a result of both processing depletion and dosing processes.

[0042] The method of using the absorbent materials in a plating system generally includes cleaning the absorbent material (or the absorbent blend of materials) of contaminants that otherwise might leach out in the electrolyte. Exemplary cleaning solutions include deionized water, diluted acid (e.g. H2SO4), or a complexing agent solution (e.g. EDTA) can be used effectively. Initiating the process with equilibration of the purified absorbent with the electrolyte relative to all chemical components (salts and additives) used in the electrolyte facilitates optimal plating results, as the concentrations are easily maintained within the processing window when initiated from an equilibrium position. This process can be performed by placing the absorbent is into the electrolyte with required concentrations of all salts and additives. As the concentration of components in the electrolyte changes, the electrolyte may periodically be analyzed and corrected so that all concentrations become the same as initial ones. During the time period between analysis processes, the absorbent material may be relied upon to maintain concentrations within the processing window. When the concentration of all additives ceases to change for a substantial period of time, this is an indication that the absorbent material has become saturated at given concentrations of additives. Further, when the total volume ratio of electrolyte absorbent remains the constant, the user can

use the equation noted above to estimate the total amount of each additive (*i.e.*, m_X, m_Y, m_{Cl}, etc.) that must be added into electrolyte to equilibrate the electrolyte-absorbent system. The same volume of electrolyte can then be supplemented with the same amount of absorbent, m_X of additive X, m_Y of Y, etc., in order to maintain the desired concentrations in the mixture for a time required to reach the adsorption equilibrium.

[0043] In another embodiment of the invention the absorbent material may be treated (saturated with additives) and then positioned placed into the electrolyte tank or in a column disposed into electrolyte loop of the electrochemical cell. The electrolyte-to-absorbent volume ratio in the electrodeposition tool can be from between about 1:1 to about 20:1. To use this system without chemical control system, this ratio will generally be relatively high, from between about 1:1 to about 1:5. To improve the stability of the bath and increase the lifetime of the electrolyte, lower volume ratios may be used.

[0044] The method of the invention may further be described as utilizing a system configured to keep the concentration of additives in a narrow window required and to minimize the accumulation of breakdown into the electrodeposition bath. The method generally includes using an absorbent material (*e.g.*, charcoal, resins, activated carbon, macroporous ion-exchange resins, polypropylene or other polymers, minerals, such as vermiculite, clay, zeolyte, silicates etc.) or a blend of absorbents in any form (beads, granules, fibers, fabrics, pads, rolls etc.), which are placed into the electrolyte for metal (Cu, Ag, etc.) electrodeposition, which contains required or desired concentrations of all additives used (chloride, suppressor, brightener, leveler, accelerator, etc). The electrolyte-to-absorbent volume ratio can be between about 1:1 and about 100:1. Periodically, as additives have been absorbed by the absorbent material and their concentration into the electrolyte drops, additional amounts of each additive are added into electrolyte so that the concentration becomes equal to the initial or desired concentration. This operation repeats while then the concentration of the additives generally does not change.

Hence, the concentration of additives in the absorbent and in the electrolyte are equilibrated.

[0045] Additionally, although embodiments of the invention illustrate a single canister, container, column, etc. being used to dispense or leach the additives into the electrolyte solution, the invention is not intended to be limited to this configuration. More particularly, embodiments of the invention contemplate that any number of containers may be used to supply the required additives to the solution. For example, separate containers may be used for each of the additives (levelers, suppressors, and accelerators), and each of the canisters may have different absorbent materials therein. The varying absorbent materials may be used to control the leaching of the particular additive, as the plating process may consume more of one additive than another, and as such, the additive with a high consumption would need to be leached at a higher rate into the solution. Thus, the absorbent material used for this additive may be configured to leach at a faster rate than other absorbent materials used for the additives that are not consumed as rapidly.

[0046] As noted above, the absorbent material may be positioned in a container having at least one fluid inlet and at least one fluid outlet. The absorbent material may include a single absorbent material, or alternatively, a combination of several absorbent materials. When a combination of materials is used, the combination of materials may be mixed together and contained within a single volume within the canister or column, or alternatively, the canister or column may be separated in a plurality of volumes and each of the volumes may be filled with an individual absorbent material, wherein each absorbent material in the respective compartments is different from the material in the other or adjacent compartments. The compartments may be separated by a fluid permeable membrane so that fluid entering the container may travel from the inlet to the outlet via the plurality of absorbent materials and one or more separation membranes. The separation membranes may further be configured to filter specific components from the electrolyte solution traveling therethrough. For example, the membranes in the

container may be configured to filter contaminants, broken down or depleted additives, or other unwanted materials from the electrolyte solution passing therethrough. The membranes may be porous filtration membranes, or alternatively, ionic membranes configured to prevent the passage of particular ions therethrough in some embodiments of the invention.

[0047] In another embodiment of the invention a plurality of the containers having the absorbent material therein may be positioned in series such that the plating solution traveling therethrough must travel through each of the containers. In yet another embodiment of the invention, a plurality of the containers may be used and placed in a parallel configuration. In this embodiment fluid solution may pass through only one of the containers having the absorbent material therein before returning to the fluid circulation loop of the plating cell. In each of the above noted embodiments, the canisters may have either a single absorbent material therein, or alternatively, a plurality of absorbent materials positioned therein. Each of the individual absorbents may be configured to absorb and leach a particular additive at a particular rate, *i.e.*, one absorbent may contain levelers, another may contain suppressors, while a third may contain accelerators.

[0048] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.